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EP-A- 0 495 547 **WO-A-95/03269**
GB-A- 949 513 **US-A- 3 527 818**

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Description

[0001] The invention relates to novel diphosphines, novel carbonylation catalysts and a process for the carbonylation of unsaturated compounds by reaction thereof with carbon monoxide and a coreactant in the presence of the novel carbonylation catalysts.

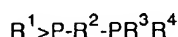
[0002] Carbonylation reactions are known in the art. For instance, in EP-A-0,495,547 several examples are disclosed wherein olefins are converted into (thio)esters, acids, anhydrides, and amides, etc., depending on the nature of the coreactant. Other examples on the synthesis of aldehydes; ketones; carboxylic acids; esters; amides and other carboxylic acid derivatives; lactones; lactams and related N-heterocycles as well as background references can be found in "Carbonylation" by Messrs H M Colquhoun, D J Thompson and M V Twigg (Plenum press 1991).

[0003] In WO-A-9503269 several examples are described wherein alkynes, viz. ethyne, 1-pentyne, propyne, phenylethyne, are converted into their respective unsaturated methylesters.

[0004] Typically, the rate of reaction is in the order of up to several hundreds moles product per mol catalyst (based on the metal) per hour. In case of internal unsaturation, the rate of reaction is even several orders lower. In other words, either relatively large amounts of catalyst are required or prolonged reaction times are involved.

[0005] The present inventors set out to provide a more active carbonylation catalyst. Surprisingly, carbonylation catalysts with high activity have been found that are obtainable by combining:

- (i) a metal cation selected from the groups 8, 9 or 10 of the Periodic Table of Elements, and
- (ii) a diphosphine of the following formula



wherein R² represents a covalent bridging group, R¹ represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms, and wherein R³ and R⁴ independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms. The diphosphines that may be used in the preparation of these carbonylation catalysts are believed to be novel too.

[0006] Tricyclo[3.3.1.1{3,7}]decane is the systematic name for a compound more generally known as adamantane. Therefore, the optionally substituted 2-phospha-tricyclo-[3.3.1.1{3,7}]decyl group will be referred to as "2-PA" group (as in 2-phosphadamantyl group) throughout the specification.

[0007] Preferably, the 2-PA group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical R⁵ of up to 20 atoms. Typical examples of R⁵ include methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl. More preferably, the 2-PA group is substituted on each of the 1, 3, 5 and 7 positions, suitably with identical radicals R⁵.

[0008] The 2-PA group has preferably additional heteroatoms other than the 2-phosphorus atom in its skeleton. Suitable heteroatoms are oxygen and sulphur atoms. Suitably, these heteroatoms are found in the 6, 9 and 10 positions.

[0009] The most preferred bivalent radical is the 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group.

[0010] Each of the monovalent radicals R³ and R⁴ may independently be selected from (substituted) hydrocarbyl groups such as, for instance, methyl, phenyl, pyridyl, or o,o-di(t-butoxy)phenyl, and (substituted) heterohydrocarbyl groups such as, for instance, trimethylsilyl or alkoxy groups. Alternatively, R³ and R⁴ may together form a bivalent radical, such as 1,6-hexylene, 1,3 or 1,4-cyclooctylene, etc. Preferably, R³ and R⁴ together form a 2-PA group, most preferably a bivalent radical identical to R¹.

[0011] The preferred ligands to be used in the carbonylation catalysts of the present invention are 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-[3.3.1.1{3,7}]decyl)ethane (DPA2); 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3,7}]-decyl)propane (DPA3); 1,2-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3,7}]-decyl)ethane, 1,3-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3,7}]-decyl)-propane, 1,2-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3,7}]-decyl)ethane and 1,3-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3,7}]-decyl)propane, DPA3 being most preferred.

[0012] The ligand so defined can be prepared in a manner similar to the process for preparing the secondary phosphine 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane disclosed in chapter 3 of "PRECIOUS METAL COMPLEXES OF SOME NOVEL FUNCTIONALISED SECONDARY AND TERTIARY PHOSPHINES" by Ms. Joanne H Downing (theses submitted to the University of Bristol on November 1992). For instance, DPA3 is prepared by adding 2,4-pentanedione to 1,3-diphosphinopropane. Asymmetric ligands may be prepared using, for instance, a diphosphine having a tertiary phosphino group and a primary phosphino group. Alternatively, they may be prepared by coupling a secondary 2-phospha-tricyclo[3.3.1.1{3,7}]decane with another secondary monophosphine or by other processes known in the art. Substituted ligands can, for example, be made using substituted 2,4-pentanediones such as perfluoro-2,4-pentanedione or 1,1,1,5,5,5-hexfluoro-2,4-pentanedione in the reaction with the phosphine.

[0013] According to the present IUPAC notation, group 8, 9 and 10 metal cations are cations of Fe, Ru, Os; Co, Rh, Ir and Ni, Pd, and Pt, respectively. These cations, as is illustrated in "Carbonylation", may each be used in the various carbonylation reactions.

[0014] Group 9 metal cations, and Group 10 metal cations (referred to in the older literature as the platinum group metal cations) have been found to provide particularly good results when used in the novel catalyst of the present invention. Especially preferred cations are cations of Rh, Pd or Pt.

[0015] Suitable sources for the metal cations may be found in "Carbonylation" and will form no problem to the person skilled in the art. Likewise, the preparation of the catalyst system (actually a precursor, the active species formed in-situ may be slightly different from that of the precursor here disclosed) follows the general recipe disclosed in the thesis by Ms J H Downing.

[0016] The catalyst systems may be used in the various carbonylation reactions described in EP-A-0,495,547 and in "Carbonylation". They particularly excel in respect of the reaction rate when applied in the additive carbonylation of unsaturated compounds, notably of ethylenically unsaturated compounds. The latter reaction, here shown for an alpha-olefin, proceeds according to the following reaction: $RCH=CH_2 + CO + HY \rightarrow RCH_2CH_2COY$; $Y = H, OH, OR, NR_2$, etc.

[0017] The additive carbonylation of internal olefins is similar. However, due to its high isomerisation activity, the products typically resemble those of the reaction with the corresponding alpha-olefin.

[0018] In other words, the catalyst systems may be used in "hydroformylation reactions", "hydrocarboxylation reactions", "hydroesterification reactions", "hydroamidation reactions", etc.

[0019] It will be understood that in such carbonylation reactions coreactants, solvents, etc. may be used. Besides, various anions may be used as counter-ion to the metal cation. Examples thereof include anions that are the conjugated base of acids having a pKa (measured at 18 °C in water) of less than 6, preferably less than 4. The anions derived from these acids do not or only weakly co-ordinate with the metal cation, by which is meant that little or no covalent interaction occurs between the anion and the cation. Catalysts based on these anions exhibit a good activity.

[0020] Suitable anions include anions derived from Bronsted acids, such as from phosphoric acid and sulphuric acid, and in particular from sulphonic acids and (halogenated) carboxylic acids, such as trifluoroacetic acid, 2,6-dichlorobenzoic acid, and 2,6-bis(trifluoromethyl)benzoic acid or trifluoroacetic acid, etc. Anions derived from sulphonic acids are particularly preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butanesulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid.

[0021] Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such

as BF_3 , $B(C_6F_5)_3$, $AlCl_3$, SnF_2 , $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, preferably having a pKa of less than 5, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalogenic acid such as HF or HCl, or a combination of a Lewis acid with an alcohol. Examples of such complex anions are BF_4^- , $SnCl_3^-$, $[SnCl_2 \cdot CF_3SO_3]^-$ and PF_6^- .

[0022] The carbonylation reaction is conveniently carried out at moderate temperatures. Accordingly, the process is suitably carried out at a temperature in the range of 30 to 200 °C, preferred temperatures being in the range of 50 to 180 °C. The reaction pressures may also vary widely. For instance, the reaction can be carried out with pressures in the range of 1 to 200 bar gauge, pressures in the range of 5 to 60 barg being preferred.

[0023] Carbon monoxide is preferably supplied in molar excess over the unsaturated compound and the coreactant "YH". In addition, the unsaturated compound and the coreactant are suitably supplied in a molar ratio within the range of 10:1 to 1:10, preferably within the range of 5:1 to 1:5, more preferably within the range of 2:1 to 1:2.

[0024] The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of 10^{-8} to 10^{-1} , preferably in the range of 10^{-7} to 10^{-2} mole atom of metal per mole of unsaturated compound are used.

[0025] For the preparation of the catalyst systems of the invention, the amount of ligand is generally applied in some excess of the amount of the metal cation, expressed as moles of ligand per mole atom of the cation. Typically the amount of ligand is selected such that per mole atom of the cation 0.5 to 10 moles of ligand are present. However, for the preferred catalyst system the active species is believed to be based on an equimolar amount of bidentate ligand per mole cation. Thus, the molar amount of bidentate ligand per mole of cation is preferably in the range of 1 to 3, more preferably in the range of 1 to 2. In the presence of oxygen, slightly higher amounts may be beneficial. The amount of the anion source may range from 0.5 to 15, preferably from 1 to 8 moles per mole of cation.

[0026] In the process of the invention, the starting materials and the formed carbonylation products may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the carbonylation reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons such as, e.g., paraffins and isoalkanes are recommended and furthermore ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole; sulphones such as sulfolane, and aromatic hydrocarbons such as toluene.

[0027] The unsaturated compound may have one or more unsaturated bonds and is preferably an olefin having from 2 to 30 carbon atoms per molecule. The unsaturated bond(s) may be internal or terminal, the cata-

lyst being particularly advantageous in the conversion of internal olefins. Particularly preferred are olefins having from 2 to 22 carbon atoms per molecule, such as ethene, propene, 1-or 2-butene, 1- or internal hexene, 1 or internal octene, diisobutylene, triisobutylene, tripropylene, internal decene, internal C₁₄ olefins, and internal C₁₅-C₁₈ olefins.

[0028] In the unsaturated compound one or more hydrogen atoms may have been substituted by other atoms, such as halogen atoms or by groups of atoms, such as hydroxyl groups, cyano groups, such as methoxy or ethoxy groups, or amino groups such as dimethyl- and diethyl-amino groups.

[0029] Another preferred category of unsaturated compounds, consists of unsaturated esters of carboxylic acids and esters of unsaturated carboxylic acids. For example, the starting material may be a vinyl ester of a carboxylic acid such as acetic acid or propanoic acid, or it may be an alkyl ester of an unsaturated acid, such as the methyl or ethyl ester of acrylic acid or methacrylic acid.

[0030] A further preferred category of unsaturated compounds, consists of cycloalkadienes, which will ordinarily refuse carbonylation. For example, the starting material may be dicyclopentadiene or norbornadiene, to give diesters, diamides or diacids, etc., which may find use as monomer in polymerization reactions.

[0031] Suitable coreactants in the additive carbonylation process of the invention include compounds comprising a nucleophilic moiety and a mobile hydrogen atom.

[0032] Preferred nucleophilic compounds include: molecular hydrogen, water and alcohols, e.g., monohydric alcohols, such as methanol, ethanol, isopropanol and 1-butanol, and polyhydric alcohols, such as ethyleneglycol, 1,4-butanediol and glycerol; thiols; primary or secondary (poly-) amines or amides, such as diethylamine, N,N-dimethyl ethylenediamine; aromatic alcohols and carboxylic acids, for example acetic acid, pivalic acid and propanoic acid. Molecular hydrogen, monohydric alcohols having from 1 to 6 carbon atoms per molecule and dihydric alcohols having from 2 to 6 carbon atoms per molecule are preferred.

[0033] 1-Butanol, methanol and 1,4-butanediol are especially preferred. The use of these compounds as coreactants enables the production of valuable carbonylation products, such as methyl propanoate, butyl propanoate and 1,4-diacetoxy butanes. These compounds are of commercial interest and may be used as solvents and in flavouring compositions and perfumes.

[0034] Another preferred class of coreactants is composed of alkylphenols, wherein one or more alkyl groups of up to 30, typically 6 to 22 carbon atoms are attached to the phenol molecule. Additive carbonylation with these coreactants produces alkylphenyl esters that may find use as synthetic lubricants in industrial application, but in particular in automotive engines.

[0035] The invention will now be further described in

the following examples, however, without restricting its scope. All experiments were carried out in a magnetically stirred 250 ml autoclave unless otherwise indicated. The abbreviations used in the Tables have the following meanings:

DPA2 = 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)ethane
DPA3 = 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propane
MSA = methanesulphonic acid

Example 1 (Synthesis of the ligands)

[0036] 4.63 Mmol diphosphinopropane was added to a solution of 27.8 mmol 2,4-pentanedione in 20 ml 5M HCl. After 1 hr stirring a white solid began to precipitate. The reaction mixture was stirred for a further 24 hrs, and then the volatile components were removed to leave a white, airstable solid product. The product was washed with water (6x 20 ml), dissolved in 20 ml dichloromethane and dried over magnesium sulphate. This solution was filtered and concentrated under vacuum to 1 ml. 10 ml pentane was added to precipitate the purified product, which was then recovered. (0.75 g, 34% yield).

[0037] ¹H NMR (400 MHz, in CD₂Cl₂), δ 1.18 (6H, s), δ 1.22 (18H, s), δ 1.4-1.9 (m, 14H); ³¹P NMR (162 MHz): δ -30.0, -30.8 ppm; mass spectrum showed m/e 472 (M⁺). These data confirm the nature of the product.

[0038] DPA2 was prepared in an identical manner, however, employing diphosphinoethane instead of diphosphinopropane.

Example 2 (Carbonylation)

[0039] The autoclave was charged with 50 ml of methanol, 0.1 mmol of palladium(II) acetate, 0.15 mmol of DPA3, and 0.2 mmol of MSA. After being flushed, the autoclave was pressurised with carbon monoxide and ethene to a partial pressure of 30 bar and 20 bar respectively. Next, the reactor was sealed. The contents of the autoclave were heated to a temperature of 90 °C and maintained at that temperature for 0.25 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by Gas Liquid Chromatography. [0040] Ethene was fully converted with 100% selectivity into methyl propanoate at an average rate of 8000 mole per mole Pd per hour (mol/mol.hr).

Example 3

[0041] Example 2 was repeated, however using 10 ml water and 40 ml of diglyme as reactant/solvent and a process temperature of 110 °C. The autoclave was cooled after 2 hours.

[0042] Ethene was fully converted with 100% selectivity into propanoic acid at an average rate of 1500 mol/mol.hr.

Example 4

[0043] Example 2 was repeated, however using 30 ml propene as olefin and a process temperature of 100 °C.

[0044] Propene was fully converted with 78% selectivity into methyl butanoate and 22% selectivity into methyl 2-methylpropanoate at an average rate of 5000 mol/mol.hr.

Example 5

[0045] Example 2 was repeated, however using 20 ml of an alpha-C₁₄ olefin feed. The autoclave was cooled after 3 hours.

[0046] The alpha-olefins were converted for 95% with 80% selectivity into linear methyl esters at an average rate of 250 mol/mol.hr.

Example 6

[0047] Example 2 was repeated, however using 20 ml of an internal-C₁₄ olefin feed, at a process temperature of 115 °C, and at a carbon monoxide pressure of 10 bar. The autoclave was cooled after 5 hours.

[0048] The internal olefins were converted for 93% with 78% selectivity into linear methyl esters at an average rate of 120 mol/mol.hr.

Comparative Example A

[0049] Example 6 was repeated, however using 1,3-bis(ditert-butylphosphino)propane as ligand, and at a carbon monoxide pressure of 10 and 30 bar, respectively. The autoclave was cooled after 10 hours.

[0050] The internal olefins were converted for only 10% with 75% selectivity into linear methyl esters at an average rate of 5 mol/mol.hr.

Example 7

[0051] Example 2 was repeated, however using 10 ml methyl 3-pentenoate as unsaturated compound, at a process temperature of 115 °C and at a carbon monoxide pressure of 15 bar. The autoclave was cooled after 6 hours.

[0052] Methyl 3-pentenoate was fully converted with 84% selectivity into linear dimethyl esters at an average rate of 100 mol/mol.hr.

Example 8

[0053] Example 2 was repeated, however using 0.1 mmol of platinum(II) acetylacetonate, 0.12 mmol of DPA3, and 0.25 mmol of MSA. Besides, the contents of the autoclave were heated to 125 °C. The autoclave was cooled after 3 hours.

[0054] Ethene was fully converted with 100% selectivity into methyl propionate at an average rate of 500

mol/mol.hr.

Comparative Example B

[0055] Example 8 was repeated, however using 1,3-bis(ditert-butylphosphino)propane as ligand.

[0056] Methyl propionate was now formed at an average rate of only 10 mol/mol.hr.

Example 9 (hydroformylation)

[0057] The autoclave was charged with 50 ml diglyme, 0.1 mmol rhodium dicarbonyl acetylacetonate, and 0.12 mmol of DPA3. After being flushed, the autoclave was charged with 15 ml propene and pressurised with carbon monoxide and hydrogen to a partial pressure of 25 bar and 25 bar each. Next, the reactor was sealed. The contents of the autoclave were heated to a temperature of 80 °C and maintained at that temperature for 0.25 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

[0058] Propene was fully converted into a mixture of butanal and 2-methylpropanal (mole ratio 48:52) at an average rate of 4000 mol/mol.hr.

Example 10

[0059] Example 9 was repeated, however using 0.1 mmol of DPA2.

[0060] Propene was now fully converted into a mixture of butanal and 2-methylpropanal (mole ratio 49:51) at an average rate of 5000 mol/mol.hr.

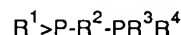
Example 11

[0061] Example 9 was repeated, however using 10 ml of vinyl acetate instead of propene, 50 ml of toluene instead of diglyme and 0.2 mmol of DPA3. Besides, the autoclave was heated to a temperature of 115 °C.

[0062] Vinyl acetate was fully converted into a mixture of 1-formylethyl acetate and 2-formylethyl acetate (mole ratio 10:1) at an average rate of 5000 mol/mol.hr.

Claims

1. A diphosphine of the following formula



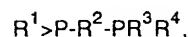
wherein R² represents a covalent bridging group, R¹ represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1 (3,7)]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by

- heteroatoms ("2-PA" group), and wherein R³ and R⁴ independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms.
2. A diphosphine as claimed in claim 1, wherein the 2-PA group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical R⁵ of up to 20 atoms.
 3. A diphosphine as claimed in claim 2, wherein R⁵ is a radical selected from methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl.
 4. A diphosphine as claimed in any one of claims 1 to 3, wherein the 2-PA group is substituted on each of the 1, 3, 5 and 7 positions, preferably with identical radicals R⁵.
 5. A diphosphine as claimed in any one of claims 1 to 4, wherein the 2-PA group has oxygen and or sulphur atoms in its skeleton, preferably in the 6, 9 and 10 positions.
 6. A diphosphine as claimed in any one of claims 1 to 5, wherein the 2-PA group is a 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group.
 7. A diphosphine as claimed in any one of claims 1 to 6, wherein R³ and R⁴ together form a 2-PA group, preferably a bivalent radical identical to R¹.
 8. A diphosphine as claimed in claim 1, selected from 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)-ethane (DPA2); 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propane (DPA3); 1,2-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)ethane, 1,3-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propane, 1,2-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)ethane and 1,3-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propane, DPA3 being most preferred.
 9. A carbonylation catalyst obtainable by combining:
 - (i) a metal cation selected from the groups 8, 9 or 10 of the Periodic Table of Elements, and
 - (ii) a diphosphine as claimed in any one of claims 1 to 8.
 10. A carbonylation catalyst as claimed in claim 9, wherein the metal cation is a group 9 metal cation or a group 10 metal cation, preferably Rh, Pd or Pt.

11. A process for the carbonylation of an unsaturated compound by reaction thereof with carbon monoxide and a coreactant, wherein a carbonylation catalyst is used as claimed in any one of claims 9 or 10.
12. A process as claimed in claim 11, wherein the unsaturated compound is ethylenically unsaturated compound of 2 to 30 carbon atoms per molecule.

Patentansprüche

1. Ein Diphosphin mit der nachstehenden Formel



worin R² eine kovalente Brückengruppe darstellt, R¹ einen zweiwertigen Rest bedeutet, der zusammen mit dem Phosphoratom, an das er gebunden ist, eine gegebenenfalls substituierte 2-Phosphatricyclo[3.3.1.1{3,7}]decylgruppe oder ein Derivat hiervon ausbildet, worin ein oder mehrere der Kohlenstoffatome durch Heteroatome ersetzt sind ("2-PA"-Gruppe), und worin R³ und R⁴ unabhängig voneinander einwertige Reste von bis zu 20 Atomen darstellen oder zusammengenommen einen zweiwertigen Rest mit bis zu 20 Atomen ausbilden.

2. Diphosphin nach Anspruch 1, worin die 2-PA-Gruppe an einer oder mehrerer der Positionen 1, 3, 5 oder 7 durch einen einwertigen Rest R⁵ mit bis zu 20 Atomen substituiert ist.
3. Diphosphin nach Anspruch 2, worin R⁵ ein unter Methyl, Trifluormethyl, Ethoxy, Phenyl und 4-Dodecylphenyl ausgewählter Rest ist.
4. Diphosphin nach einem der Ansprüche 1 bis 3, worin die 2-PA-Gruppe an jeder der Positionen 1, 3, 5 und 7 substituiert ist, vorzugsweise durch identische Reste R⁵.
5. Diphosphin nach einem der Ansprüche 1 bis 4, worin die 2-PA-Gruppe in ihrem Skelett Sauerstoff- oder Schwefelatome aufweist, vorzugsweise in den Positionen 6, 9 und 10.
6. Diphosphin nach einem der Ansprüche 1 bis 5, worin die 2-PA-Gruppe eine 2-Phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantylgruppe ist.
7. Diphosphin nach einem der Ansprüche 1 bis 6, worin R³ und R⁴ zusammengenommen eine 2-PA-Gruppe ausbilden, vorzugsweise einen zu R¹ identischen zweiwertigen Rest.
8. Diphosphin nach Anspruch 1, ausgewählt unter 1,

2-P,P'-Di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-[3.3.1.1{3.7}]decyl)ethan (DPA2); 1,3-P,P'-Di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]-decyl)propan (DPA3); 1,2-P,P'-Di-perfluor(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]-decyl)ethan, 1,3-P,P'-Di-perfluor(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propan, 1,2-P,P'-Di-(2-phospha-1,3,5,7-tetra(trifluormethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)ethan und 1,3-P,P'-Di-(2-phospha-1,3,5,7-tetra(trifluormethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}]decyl)propan, wobei DPA3 am meisten bevorzugt ist.

9. Carbonylierungskatalysator, erhältlich durch Vereinigen

(i) eines Metallkations, ausgewählt aus den Gruppen 8, 9 oder 10 des Periodensystems der Elemente, mit
(ii) einem Diphosphin nach einem der Ansprüche 1 bis 8.

10. Carbonylierungskatalysator nach Anspruch 9, worin das Metallkation ein Gruppe 9-Metallkation oder ein Gruppe 10-Metallkation ist, vorzugsweise Rh, Pd oder Pt.

11. Verfahren zur Carbonylierung einer ungesättigten Verbindung durch deren Umsetzung mit Kohlenmonoxid und einer Co-Reaktionskomponente, worin ein in einem der Ansprüche 9 oder 10 beanspruchter Carbonylierungskatalysator verwendet wird.

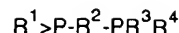
12. Verfahren nach Anspruch 11, worin die ungesättigte Verbindung eine ethylenisch ungesättigte Verbindung mit 2 bis 30 Kohlenstoffatomen pro Molekül ist.

13. Verfahren nach Anspruch 12, worin die ethylenisch ungesättigte Verbindung ein α - oder inneres Olefin mit 2 bis 22 Kohlenstoffatomen pro Molekül oder ein Cycloalkadien ist.

14. Verfahren nach einem der Ansprüche 11 bis 13, worin die Co-Reaktionskomponenten molekularer Wasserstoff, einwertige Alkohole mit 1 bis 6 Kohlenstoffatomen pro Molekül, zweiwertige Alkohole mit 2 bis 6 Kohlenstoffen pro Molekül und Alkylphenole sind.

Revendications

1. Diphosphine selon la formule suivante :



dans laquelle R^2 représente un groupe lié de manière covalente, R^1 représente un radical bivalent qui, avec l'atome de phosphore auquel il est attaché, est un groupe optionnellement substitué de 2-phosphatricyclo[3.3.1.1{3,7}]décyle ou un dérivé de celui-ci dans lequel un ou plusieurs atomes de carbone sont remplacés par des hétéroatomes (groupe "2-PA"), et dans laquelle R^3 et R^4 représentent indépendamment des radicaux univalents ayant jusqu'à 20 atomes ou qui forment ensemble un radical bivalent ayant jusqu'à 20 atomes.

2. Diphosphine suivant la revendication 1, dans laquelle le groupe 2-PA est substitué sur une ou plusieurs positions 1, 3, 5 ou 7 avec un radical monovalent R^5 ayant jusqu'à 20 atomes.

3. Diphosphine suivant la revendication 2, dans laquelle R^5 est un radical choisi parmi le méthyle, le trifluorométhyle, l'éthoxy, le phényle et le 4-dodécylphényle.

4. Diphosphine suivant l'une quelconque des revendications 1 à 3, dans laquelle le groupe 2-PA est substitué sur chacune des positions 1, 3, 5 et 7, de préférence avec des radicaux R^5 identiques.

5. Diphosphine suivant l'une quelconque des revendications 1 à 4, dans laquelle le groupe 2-PA a des atomes d'oxygène et/ou de soufre dans son squelette, de préférence en position 6, 9 et 10.

6. Diphosphine suivant l'une quelconque des revendications 1 à 5, dans laquelle le groupe 2-PA est un groupe 2-phospha-1,3,5,7-tétraméthyl-6,9,10-trioxadamantyle.

7. Diphosphine suivant l'une quelconque des revendications 1 à 6, dans laquelle R^3 et R^4 forment ensemble un groupe 2-PA, de préférence un radical bivalent identique à R^1 .

8. Diphosphine suivant la revendication 1, sélectionnée parmi le 1,2-P,P'-di(2-phospha-1,3,5,7-tétraméthyl-6,9,10-trioxatricyclo-[3.3.1.1{3,7}]décyl)éthane (DPA2); le 1,3-P,P'-di-(2-phospha-1,3,5,7-tétraméthyl-6,9,10-trioxatricyclo[3.3.1.1{3,7}]décyl)propane (DPA3); le 1,2-P,P'-di-perfluoro(2-phospha-1,3,5,7-tétraméthyl-6,9,10-trioxatricyclo-[3.3.1.1{3,7}]décyl)éthane, le 1,3-P,P'-di-perfluoro(2-phospha-1,3,5,7-tétraméthyl-6,9,10-trioxatricyclo[3.3.1.1{3,7}]décyl)propane, le 1,2-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluorométhyl)-6,9,10-trioxatricyclo-[3.3.1.1{3,7}]décyl)éthane et le 1,3-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluorométhyl)-6,9,10-trioxatricyclo[3.3.1.1{3,7}]décyl)éthane.

1.1{3,7}décyl)propane, le DPA3 étant le plus préféré.

9. Catalyseur de carbonylation obtenu par la combinaison : 5
- (i) d'un cation métallique choisi à partir des groupes 8, 9 ou 10 du Tableau Périodique des Eléments, et
- (ii) d'une diphosphine suivant l'une quelconque des revendications 1 à 8. 10
10. Catalyseur de carbonylation suivant la revendication 9, dans lequel le cation métallique est un cation métallique du groupe 9 ou un cation métallique du groupe 10, de préférence du Rh, du Pd ou du Pt. 15
11. Procédé pour la carbonylation d'un composé insaturé par réaction de celui-ci avec du monoxyde de carbone et un coréactif, **caractérisé en ce que** le catalyseur de carbonylation est utilisé suivant l'une des revendications 9 ou 10. 20
12. Procédé suivant la revendication 11, **caractérisé en ce que** le composé insaturé est un composé éthyléniquement insaturé de 2 à 30 atomes de carbone par molécule. 25
13. Procédé suivant la revendication 12, **caractérisé en ce que** le composé éthyléniquement insaturé est une oléfine alpha- ou interne ayant de 2 à 22 atomes de carbone par molécule, ou un cyclo-alcadiène. 30
14. Procédé suivant l'une quelconque des revendications 11 à 13, **caractérisé en ce que** le coréactif est de l'hydrogène moléculaire, des alcools monohydriques ayant de 1 à 6 atomes de carbone par molécule, des alcools dihydriques ayant de 2 à 6 atomes de carbone par molécule et des alkylphénols. 35 40

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